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Studies of structural and dielectric properties of $NaSr_5TiNb_9O_{30}$

H Sharma, Kiran Kumari* and N K Singh
PG Teaching Centre in Physics, H. D Jain College,
Arrah-802 301, Bihar, India

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Abstract : The polycrystalline samples of $NaSr_5TiNb_9O_{30}$ (subsequently referred to as NST) which belongs to a ferroelectric oxide family of tungsten-bronze structure, were prepared by high temperature solid-state reaction process. Preliminary X-ray analysis of the samples yielded lattice parameters $a = 8.7134$ Å, $b = 11.7606$ Å and $c = 12.5004$ Å and also formation of single phase compound. Detailed studies of dielectric constant and loss as a function of temperature and frequency and electrical conductivity show transition at 160°C which is quite different from other members of the family.

Keywords : Tungsten-bronze structure, X-ray diffraction, dielectric constant

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Since the discovery of ferroelectricity [1] in $BaTiO_3$, a large number of ferroelectric oxides of pervoskite [2,3] and tungsten-bronze (TB)-type structures [4,5] have been studied. Some niobates with TB structure such as barium sodium niobate [6], potassium lanthanum niobates [7] *etc.* are now considered to be very interesting and attractive because of their wide industrial applications. The TB-type structure consists of a complex array of distorted BO_6 octahedra sharing corners in such a way that three different types of interstices (A_1, A_2, B_1, B_2 and C) are available for cation substitution [8]. The general formula commonly used for this family is $(A_1)_4\ (A_2)_2\ (C)_4\ (B_1)_2\ (B_2)_8\ O_{30}$ in which a wide variety of substitution can be made. The polar axis of most of the members of the TB-family is normally c-axis. Also it has been found that some of the members of this family have transition temperatures well above the room temperature with diffuse phase transition [9]. Though some work has been done on NST [10], no systematic X-ray and dielectric studies have been reported on the same so far. We therefore in this paper, report

*Present Address : Post Graduate Teacher (PGT) in Physics, K V Sonepur-841 101, Bihar, India

preliminary structural and detailed electrical (dielectric constant [ε], loss [tan δ] and electrical conductivity) properties of the $NaSr_5TiNb_9O_{30}$ (NST) compound.

The polycrystalline NST compound was synthesized using high-temperature solid-state reaction techniques from the component oxides and carbonates : TiO_2 (99%, s.d. Fine Chem Pvt. Ltd), Nb_2O_5 (99.9% SMP), Na_2CO_3 (99.9% SM Chemicals) and $SrCO_3$ (AG). These oxides/carbonates were thoroughly mixed in agate mortar in air atmosphere for 5 hours to get homogeneous mixture. The NST was obtained by repeated mixing and calcination at 1000°C for about 28 hours. The formation of the prepared compound was checked by X-ray diffraction technique.

The fine homogeneous powder of NST was used to make pellets (diameter 10.3 mm and thickness 2.75 mm) at the pressure of 5×10^7 kg/cm^2 using hydraulic press. These pellets were sintered in air atmosphere at 1100°C for 10 hours. The X-ray diffraction (XRD) pattern of sintered pellet was obtained using X-ray powder diffractometer [Philips PW-1710, Holland] with CuK_α (λ = 1.5418 Å) radiation in the wide range of Bragg angle ($20° \leq 2\theta \leq 70°$). A few of the sintered disc samples were polished with fine emary paper to make the surfaces flat, smooth and parallel for dielectric measurements. The two flat surfaces were electroded with silver paste. Measurements of dielectric constant (ε) and loss (tan δ) were carried out on a GR-1620 AP capacitance measuring assembly as function of frequency (500 Hz–10 KHz) at room temperature and also as a function of temperature from 190°C up to 220°C using a laboratory made three-terminal sample holder and silver paste as electrode terminal.

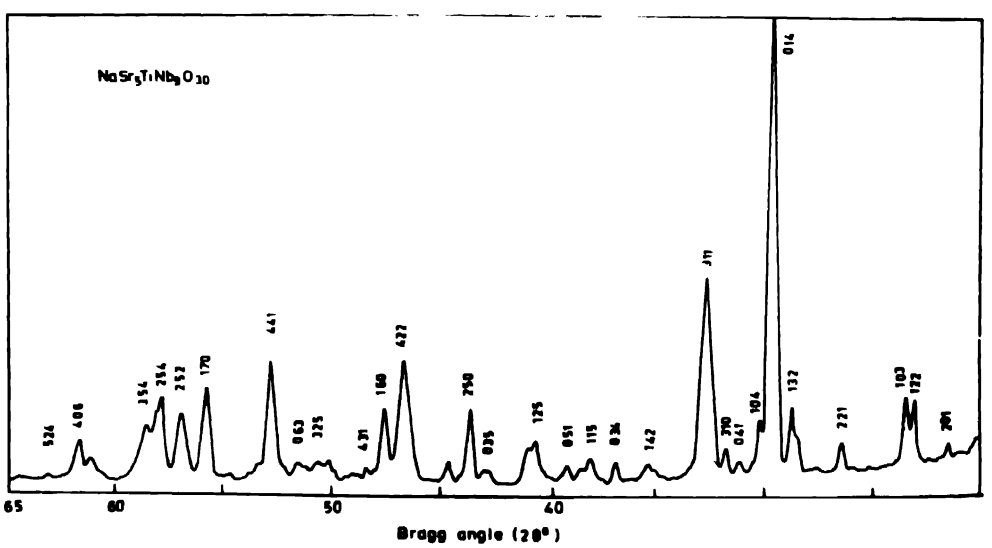

Figure 1. Room temperature X-ray diffraction pattern of $NaSr_5TiNb_9O_{30}$

The sharp and single diffraction peaks of the sample (Figure 1) suggest the formation of single phase compound. All the peaks were indexed from their observed d values. Then lattice parameters of a selected orthorhombic cell were determined using a

standard computer programme package entitled 'powder'. The lattice parameters obtained were refined with 32 reflections using the least-squares method giving : a = 8.7130 Å, b = 11.7606 Å and c = 12.5004 Å. Comparison of observed and calculated d-values (Table 1) shows a very good agreement in them suggesting the correctness of the preliminary crystal data.

Table 1. Comparison of observed and calculated d-values (Å) of some reflections of NST at room temperature.

h	k	l	d_{obs}	d_{cal}	I/I_0
1	2	0	4 8742	4 8742	4
2	0	1	4.1140	4.1140	10
1	2	2	3.8436	3.8436	9
1	0	3	3.7858	3 7841	9
2	2	1	3.3709	3 3709	10
1	3	2	3 1040	3 1033	7
0	1	4	3.0180	3 0203	100
1	0	4	2 94916	2 9592	15
0	4	1	2.8698	2 8620	7
3	1	0	2 8143	2 8298	10
3	1	1	2.7450	2 7506	41
1	4	2	2 5445	2.5439	7
0	3	4	2 4422	2 4432	8
1	1	5	2.3678	2.3645	8
0	5	1	2 3083	2 3116	6
1	2	5	2 2278	2 2258	11
0	3	5	2.1071	2 1075	6
2	5	0	2.0713	2 0697	16
1	0	6	2.0294	2 0273	6
4	2	2	1 9450	1 9416	26
1	6	0	1.9118	1.9123	16
4	3	1	1.8828	1.8824	5
3	2	5	1.8019	1.8035	6
0	6	3	1 7725	1.7737	6
4	4	1	1 7338	1.7335	24
1	7	0	1 6485	1 6496	2
5	2	2	1.6171	1 654	15
2	5	5	1.5941	1 5942	18
3	5	4	1.5777	1 5778	8
4	3	5	1.5148	1 5148	7
4	0	6	1.5046	1.506	10
5	2	4	1.4735	1 4733	4

With the limited reflections, it was not possible to find out the space group of NST. The linear particle size (L) of the sample obtained using the following Scherrer's equation with low and high angle of reflection [11]

$$L = \frac{0.89\lambda}{B_{1/2}\cos\theta} \quad (B_{1/2} = \text{half peak width})$$

was found to be 215 Å.

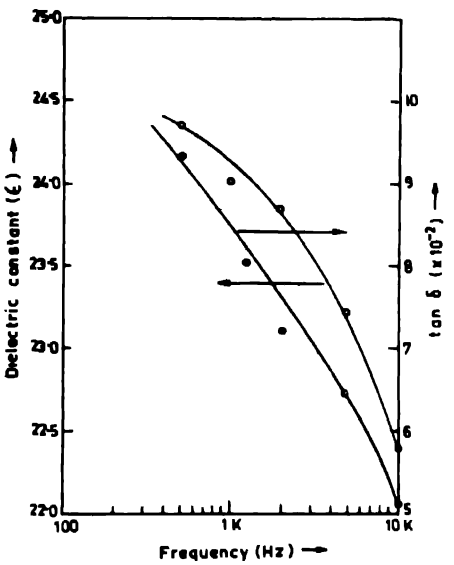

Figure 2. Variation of dielectric constant (ε) and loss (tan δ) of NST as function of frequency at room temperature

Figure 2 shows the variation of ε and tan δ with frequency indicating a normal behaviour of a dielectric. Figure 3 gives the variation of ε and tan δ both with temperature

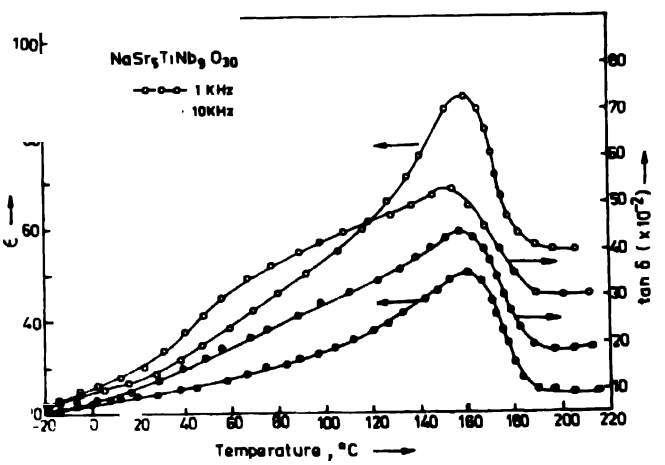

Figure 3. Variation of dielectric constant (ε) and loss (tan δ) of NST as a function of temperature at 10 KHz and 1 KHz.

at two different frequencies (1 KHz and 10 KHz). It was found that the value of ε was almost constant from liquid nitrogen temperature to –20°C, and, therefore, the same has not been shown in the figure. The value of ε, however, increases slowly upto 60°C and then increases fast upto its maximum value (*i.e.* 42 at 10 KHz and 82 at 1 KHz) at 160°C. These values decrease rapidly as the temperature is raised. This shows a normal behaviour of a ferroelectric material [12]. The presence of dielectric anomaly at 160°C however, points towards the possibility of material being ferroelectric. In fact, the measurement of spontaneous polarization as a function of temperature is required to confirm the ferroelectric nature of this compound unambiguously.

The ac conductivity was calculated from the formula $\sigma = \omega\varepsilon_0\varepsilon \tan\delta$ where ε_0 = vacuum dielectric constant and ω = angular frequency. The activation energy was obtained

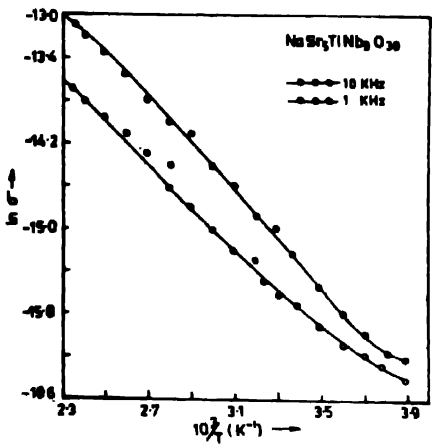

Figure 4. Variation of conductivity (ln σ) of NST as a function of inverse of temperature ($1/T$).

from the graph of ln σ *vs* $1/T$ (Figure 4). In the temperature range 30–100°C, figure gives the activation energy 0.17 eV.

Finally, it is inferred that the NST compound has orthorhombic structure at room temperature with normal ferroelectric phase transition at 160°C.

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